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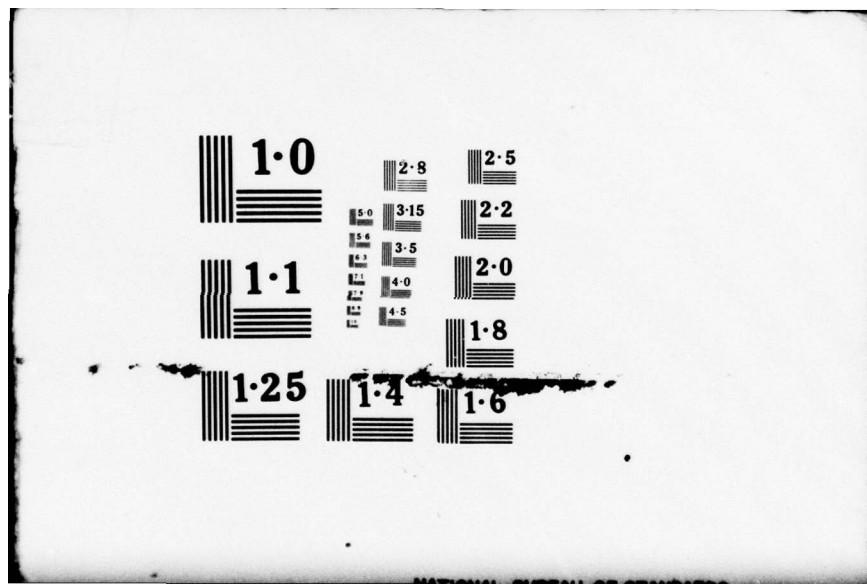
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CALIFORNIA INSTITUTE OF TECHNOLOGY

Daniel and Florence Guggenheim Jet Propulsion Center
Kármán Laboratory of Fluid Mechanics and Jet Propulsion

Division of Engineering and Applied Science

FINAL REPORT

Contract AFSOR-74-2694

Combustion Dynamic Processes

Associated with Chemical Advanced Lasing Systems

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ABSTRACT

A four-year program has been devoted to some problems of combustion dynamics arising in chemical lasers. The subjects treated are common to any system to be used as the basis for a laser, but the CS₂/O₂ system has been adopted as the particular example. This work has been generally concerned with the combined influences of molecular kinetics, chemical kinetics and fluid mechanics. Both experimental and analytical efforts have been directed to pre-mixed flames and the reacting laminar mixing layer, all at low speeds (< 10 m/sec) and low pressures (< 20 torr). Data for the flame speeds of pre-mixed flames have been used to verify the simplified kinetics mechanism deduced early in this program. Observations of spontaneous emission have been used to deduce flow temperatures; and the populations and rates of populations for the vibrational levels of carbon monoxide produced in the reactions O + CS → CO + S. Those results, taken over broad ranges of mixtures and flow conditions, and combined with analytical work, have shown why, for this system, combustion in the laminar mixing layer is greatly inferior to pre-mixed flames for producing stimulated emission.

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I. INTRODUCTION

This report summarizes a four year program devoted to some problems arising in chemical lasers. The subjects treated are common to any system which is to be used as the basis for a chemical laser, but the CS_2/O_2 system has been adopted as the special example studied in this work.

The program has been devoted to problems which may generally be characterized as combustion dynamics, concerned with the combined influences of molecular kinetics, chemical kinetics and fluid mechanics. Ultimately it is the radiation field which is of interest, both as the output of a laser and as a means of diagnostics to study the details of the flow field. For the conditions under which we have performed our experiments, the amount of energy emitted and contained in the radiation field is a small proportion of the total energy released in the combustion processes, so the influence of radiation on the flow field may be ignored.

Carbon disulfide (CS_2) and oxygen burn according to a branching chain mechanism and indeed this combination was one of the first systems treated with the principles of chemical kinetics during the 1930's. One of the intermediate reactions is a three-body exchange process involving atomic oxygen and carbon monosulfide, $\text{O} + \text{CS} \rightarrow \text{CO} + \text{S}$. The carbon monoxide is produced vibrationally excited and exhibits a total population inversion over a range of vibrational levels below the tenth or eleventh. It is this production of carbon monoxide which provides the emitted radiation used in much of this work as a means of examining the flow field.

To date the CS_2/O_2 system has not proven to be useful for a practical laser because the power produced is too low. Only recently has the group at McDonnell-Douglas succeeded in producing the largest power so far reported, 500 watts. For studying fundamental problems, on the other hand, the CS_2/O_2 system is very attractive, especially by comparison with the more familiar hydrogen/flourine systems. The most obvious advantage is that the reactants and products are much more easily, and therefore more cheaply, handled. For work in a university those are very persuasive attributes. A characteristic important to our work is that carbon disulfide and oxygen may be continuously burned easily either as a pre-mixed or as an unmixed system. We have therefore been able to compare the behavior of a single combination of reactants in both pre-mixed and unmixed configurations which may be used in chemical lasers. In contrast, almost all work with continuously reacting hydrogen/flourine systems has been with the reactants initially unmixed. The central problem in that case is the reacting mixing layer.

The program reported here therefore divides naturally into two parts, devoted respectively to problems related to premixed combustion and to problems related to a reacting mixing layer. Chronologically, the pre-mixed case was treated first, but as later remarks will emphasize, the two parts of the program are strongly inter-dependent. Throughout this work, experimental and analytical efforts proceeded simultaneously.

In broad outline the intent of this work has been to progress from problems of pre-mixed combustion; to problems associated with a

laminar reacting mixing layer; and ultimately to address the more difficult questions posed by a turbulent reacting mixing layer. The last part remains as a subject for future work. All of the accomplishments to date have either appeared in publications or are covered in reports currently being prepared. No detailed technical discussions will be included here and we shall confine ourselves here to a rather general coverage of the development of the program and the major achievements.

II. KINETICS AND THE PRE-MIXED COMBUSTION OF CS₂/O₂

When this program started, it was already known from the works of others that the combustion of carbon disulfide and oxygen could be used as the basis for a continuously operating purely chemical laser. Pre-dating that result, much had been done with many detailed aspects of the associated chemical kinetics. The rate constants had been measured or estimated for many of the chemical reactions which may occur in this system. Because of the great interest in electrically excited carbon monoxide lasers, much was also known about the molecular energy transfer processes for carbon monoxide. Subsequent to the discovery of the CS₂/O₂ laser, several measurements had been made of the distribution of vibrationally excited carbon monoxide produced in the crucial reaction O + CS → CO + S.

Consequently, a great deal of the necessary information about microscopic processes was already available. One purpose of this program has been to incorporate that information in the framework of combustion dynamics encompassing the macroscopic behavior of a continuously reacting system.

The first step was a thorough survey of the literature covering the known chemistry and chemical kinetics. This has been published as part of ref. 1. For our general use, the equilibrium composition and flame temperature for CS₂/O₂ were calculated over the entire range of mixture ratio; we used the NASA program CEC-72 (NASA SP-273).

More importantly, considerable effort was expended to produce the simplest possible kinetics mechanism. For pre-mixed combustion with a lean mixture at low pressures (less than atmospheric, but possibly higher) a scheme of four reactions is the simplest. It is necessarily a branching chain, because the CS_2/O_2 exhibits well-known explosion limits. The reduction from 32 possible reactions to four was accomplished first by arguments based on rates and known chemical behavior. Later the conclusion was verified by screening the set with a kinetics computer program. For this we used the GKAP (Generalized Kinetics Analysis Program) developed by Ultrasystems, Inc., and provided to us by Mr. G. R. Nickerson. We should note that other researchers independently proposed the same kinetics mechanism at about the same time, but, so far as we are aware, without the thorough justification reported in ref. 1.

The kinetics mechanism was tested first by using it to check qualitatively the explosion limits which had been reported by others. More importantly, we carried out analyses of the flame structure and flame speed for a laminar pre-mixed CS_2/O_2 flame. Several approximate calculations were completed (ref. 1) but the most significant is the thermal theory incorporating the kinetics just described (refs. 1 and 2).

Numerical calculations of the flame speed provided reasonable values, and very substantial justification for the simple branching chain kinetics mechanism involving four reactions. But the analyses alone are insufficient to provide satisfactory verification. An extensive experimental program was followed to measure the flame speed and to

gain as much information as possible about the flame structure. For this purpose a multi-slot injector was designed and operated. The reactants, CS_2 and O_2 , are initially unmixed and exhaust through small slots, alternately providing fuel and oxidizer. A screen placed very close to the exit plane produces thorough mixing before combustion. Burning takes place in a half-cylindrical front downstream of the injector, very closely a two-dimensional flow. Locally the front is one-dimensional and photographs of the flame may be used to infer the flame speed.

Results were obtained over a rather broad range of pressure and flow rates (refs. 2-4). These data have been compared favorably with the computations (ref. 2) and constitute the strongest available justification for the kinetics mechanism developed earlier.

During this part of the program a few measurements of temperature were taken, using a thermocouple. These are necessarily crude owing to the difficulties associated with interpreting the performance of a thermocouple placed in a high temperature reactive atmosphere. However, the results seem to support qualitatively the calculations of the flame structure. The photographs as well provide estimates of the reaction zone in rough agreement with the calculations.

A major part of the experimental work during this part of the program was devoted to observation of spontaneous emission from carbon monoxide. There is a difficult signal/noise problem. As others have found, available detectors are inadequate to obtain useable data for the fundamental emission which falls in a wavelength range around five microns. The signal/noise ratio for a PbS detector used to measure

first overtone emission near 2.5μ is about a factor of ten better than that for a Ge/Au detector used to measure fundamental emission.

Owing to the low intensity of the emission, it was necessary to use a rather large field of view. The spatial resolution of our data was not good: we have not been able to obtain any results for the structure of the reaction zone for the relatively thin flames studied. All the observations referred to here are averages over a field approximately one centimeter in diameter.

From measurements of the relative intensities of the overtone transitions, from $v = 2 \rightarrow 0$ up to $v = 20 \rightarrow 18$, the relative population $0 \leq v \leq 20$ may be directly determined; the only additional information required is the Einstein coefficients, which are well-known for carbon monoxide. The distribution of carbon monoxide over the vibrational levels is not well-approximated by a Boltzmann distribution. Merely as a crude measure of the non-equilibrium character of the populations, least-squares fits to Boltzmann distributions produced vibrational temperatures in the range 9200°K - 11900°K . The flame temperature lies between 1700°K and 2300°K . Hotter flames consistently gave higher vibrational temperatures, roughly suggestive of greater partial inversion. In no case was a total inversion observed.

The rates of population into the various vibrational levels can also be deduced from the data for spontaneous emission, but other rate processes must be accounted for. In particular both vibrational/vibrational and vibrational/translational energy transfer must be included. With several additional approximations, the rates of population were computed

from the data. The rate was found to be a maximum for the fifteenth level, which is two levels higher than for the maximum found by previous workers using data taken at lower temperatures. Ours were the first results for a CS_2/O_2 flame.

During this part of the program we did not try to construct a laser using a pre-mixed system. (See the following section for later efforts.) Our intent was to acquire all the necessary information about the chemistry, chemical kinetics and molecular energy transfer; to establish the correct kinetics mechanism; to perform the experiments necessary to support the proposed kinetics; and to make the spectroscopic measurements providing results for the populations and rates of population of the vibrational levels of carbon monoxide in a pre-mixed flame. All of this work was necessary preparation and foundation for the subsequent work on the reacting laminar mixing layer.

-9-

III. THE LAMINAR MIXING LAYER AND COMBUSTION OF CS₂/O₂

The reacting mixing layer is a fundamental problem of very general interest in many sorts of combustion systems. Our work in this part of the program is concerned with rather special conditions, low Mach number and low Reynolds number. These are restrictive so far as practical combustion devices are concerned, but they define the logical next step.

Even though the flow is definitely laminar, the mixing layer is a difficult problem because of the complicated chemistry and the large amount of energy release. Our first visual observations, using a small injector showed that the reaction zone cannot be collapsed to a simple flame sheet (ref. 6). Thus, preliminary notions that the flow might be treated with a one-dimensional approximation had to be discarded.

During this second part of this program, covering the last three years, the greater proportion of effort has been experimental. Most of the data and observations have been taken for the flow from a double-slot injector, producing a mixing layer between parallel streams of CS₂ and O₂ with variable amounts of inert diluents. The slots were 1.3 cm x 20 cm and the injector was mounted in a vacuum chamber 30 cm x 45 cm x 110 cm with various ports for gas inlets and exhaust and for making spectroscopic measurements. The injector was mounted on a platform which could be translated axially and transversely. This allowed photographs and spectroscopic measurements to be taken over most of the flow field downstream of the injector, but with the optical axis fixed

relative to the chamber. Details of the apparatus and most of the work to be described now appear in reference 7.

A limited number of measurements were taken with thermocouples. The results qualitatively verified the temperature field determined from measurements of the overtone emission from carbon monoxide vibrational transitions.

The major result of this effort is the conclusion that, for the CS_2/O_2 system, the low speed mixing layer offers a very poor environment for producing stimulated emission. There are at least two important reasons, both arising from the chemistry: production of COS introduces a species which unfavorably absorbs vibrational energy from the excited carbon monoxide molecules; and there is sufficient time for the carbon monoxide to be oxidized to carbon dioxide. The GKAP program mentioned earlier has been used to study the formation of carbon dioxide, and of COS which acts efficiently to de-activate vibrationally excited CO.

We have been unable to operate the mixing layer as a laser for the reasons cited above; this negative conclusion is therefore understood. On the other hand, we have produced laser output with a pre-mixed configuration for which also observations of spontaneous emission have been made. The inversion among the vibrational populations, inferred from the emission spectra, is consistent with the spectrum measured for the laser. In this effort we have also examined the influence of N_2O which has long been known to improve the performance of the CS_2/O_2 chemical laser.

Tests have been conducted with N_2O added to both the pre-mixed flame and the mixing layer. In all cases the spontaneous emission has

been measured. Our data show that there is evidence of oxidation of CO by N₂O, more pronounced in the mixing layer. Participation of N₂O chemically has been established by observation of the production of CO₂ and by a few measurements of the flame speed. But the main favorable influence of N₂O is as a de-activator of lower levels in the CO vibrational transitions producing stimulated emission. This possibility has long been recognized by others as well, but we believe that our results constitute the first direct quantitative evidence.

As part of this program, spectroscopic data have been taken also for reacting mixing layers for the systems H₂S/O₂, COS/O₂ and CO/O₂. The results have been helpful in clarifying certain aspects of the CS₂/O₂ problem, but will not be discussed here (see ref. 7).

Spectra of spontaneous emission have been used to determine profiles of temperature and populations of vibrationally excited CO through the two-dimensional field of the mixing layer. It happens that the lower overtone transitions (roughly up to v = 6 - 4) produce an equilibrium spectrum. This follows upon comparison of the observed spectrum with a theoretical spectrum calculated with the influence of the optical system included. From the relative intensities associated with these transitions, the temperature and population densities can be deduced. Some care is required because of the high temperatures which cause overlapping (in wavelength) of the spectra for the individual transitions.

We have used an option in the GKAP code cited in §II above, to carry out approximate calculations of the mixing layer based on the one-dimensional approximation. Entrainment in the layer is included and the chemical kinetics and the vibrational kinetics are treated very

thoroughly. The results show that a population inversion is produced, in vibrationally excited CO, only for a short distance downstream of the splitter plate. This conclusion is not inconsistent with our experimental observations but the quantitative features are very unsatisfactory.

Analyses are therefore in progress to predict the behavior in the two-dimensional mixing layer. These involve the boundary layer approximation for the flow equations. The kinetics is approximated either as a simple overall single reaction or, more realistically, by the scheme of four reactions described earlier. In order to simplify this work, the calculations of the flow and kinetics are first carried out with CO treated as a single species. Subsequently the production of carbon monoxide in the vibrational levels, and the vibrational kinetics are treated. Only preliminary results have been obtained at this writing; a more complete coverage will be included in reference 7.

The behavior of the CS_2/O_2 mixing layer is similar, in some respects, to that for combustion of hydrocarbons, studied a few years ago, but apparently quite different from that of the H_2/F_2 system. However, the latter has been examined at high speeds ($M > 1$) for the most part, and there seems to be no data for conditions comparable to those we have used in this program. Because the kinetics mechanisms are different, it should not be surprising that the global combustion dynamics are different. For example, here we have noted the importance of the oxidation of carbon monoxide, $\text{CO} \rightarrow \text{CO}_2$, which destroys the species producing stimulated emission. The corresponding process $\text{HF} \rightarrow \text{HF}_2$ does not occur in the H_2/F_2 system.

In the broad context of chemical laser systems, understanding the behavior of the CS_2/O_2 mixing layer may well be important for clarifying other cases of branching chain kinetics, or showing similar chemical behavior in other respects.

IV. INFLUENCE OF AN ELECTRIC DISCHARGE ON
CHEMICAL PRODUCTION OF VIBRATIONALLY
EXCITED CARBON MONOXIDE

Because of the emphasis on combustion dynamics in this program, we have not until recently pursued potentially interesting aspects involving electrical discharges. During the last few months of the final year we have begun examining a problem which seems not previously to have been treated. We have constructed apparatus to study the behavior of premixed combustion of CS_2/O_2 in the presence of a D.C. electric discharge. The purpose is to learn how collisional processes involving electrons may alter the populations of vibrationally excited carbon monoxide produced in the reaction $\text{O} + \text{CS} \rightarrow \text{CO(v)} + \text{S}$.

Virtually all of the experimental techniques, and much of the analysis of kinetics, developed during the past four years are immediately useful. In particular, preliminary observations of the overtone spectra show that there is indeed an influence of the discharge. That there should be an effect follows from the fact that electrically excited CO lasers have very high efficiency and power output. A practical purpose of this work is to determine whether features of chemical and electrical lasers may be combined in a single hybrid device. This work is currently unsupported and will eventually be reported in reference 8.

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